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Plasmochemical process for the production of niobium and tantalum nanopowders

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Abstract. Niobium and tantalum powders used in modern manufacturing are materials with nanostructure. The authors have studied and optimized the process of the production of niobium and tantalum nanopowders (adjusted in the range of the particle size of 20–150 nm) at pilot scale. The process is based on the reduction reaction of pentachlorides of tantalum and niobium with hydrogen in a plasma generator at about 3500 K. To stabilize the structure and adjust the granulometric composition of the produced nanopowders thermal treatment at 1373 K under vacuum was applied. The powders are characterized by very high purity with regard to oxygen and metallic admixtures and by low bulk density (0.1–0.3 g/cm^3). The specimens had a high specific surface area (10–30 m^2/g). The process of compacting and sintering of powders was tested at temperatures from 1173 to 1373 K. The porosity of the specimens was 0.55–0.75 from the theoretical. The pore diameter was adjusted to 0.5–0.05 μm.

Key words: niobium, tantalum, pentachlorides, reduction, plasmatron, nanopowders.

INTRODUCTION

Fast development of the electronic industry has highlighted the benefits of refractory metals (niobium and tantalum) as construction and functional materials. To meet modern quality standards, tantalum and niobium nanopowders should be characterized by advanced physico-technological parameters and a modified structure. Niobium and tantalum have a complex of unique physical and chemical properties. Despite the similarity of the two metals in some properties, tantalum has several advantages, for example, compatibility with the human biological tissue.

In 2007 the electronic industry used about half of the global production of tantalum, mainly in the form of powder and wire in minicapacitors production for high-tech application areas: telecommunication, production of memory cards, electronic schemes, medical implants, autodefrillebrators, etc. The USA, where about 60% of tantalum goes for capacitors production, has become the greatest consumer and importer of this metal [1,2].

Tekna Plasma Systems Inc. (Canada) and QinetiQ (UK) are the leading companies in the field of plasmochemical applications. Their scientific activities are focused on a wide spectrum of the production and use of nanopowders. For example, Tekna Plasma Inc. uses high-frequency induction plasma for nanomaterials (20–100 nm) synthesis [3]. Studies in this direction are also carried out in the Plasma Process Laboratory of the Institute of Inorganic Chemistry of Riga Technical University [4]. The company Neomat Co, applying an elaborated plasmatechnology, produces nanopowders of a very wide scale [5]. In Estonia plasmochemical production of niobium and tantalum is using an environmentally friendly technology. Before 1991 pilot and full-scale tests of the production of niobium and tantalum nanopowders using the plasmochemical method in arc plasmatrons were carried out in Silmet JSC (Fig. 1a).

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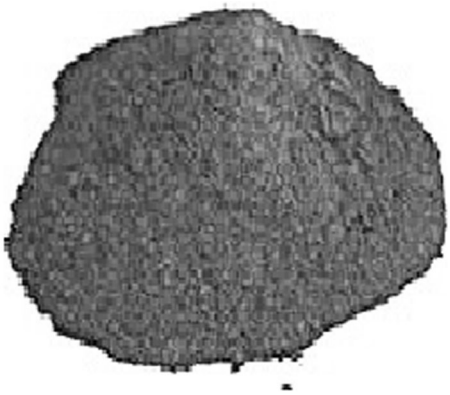
(a)



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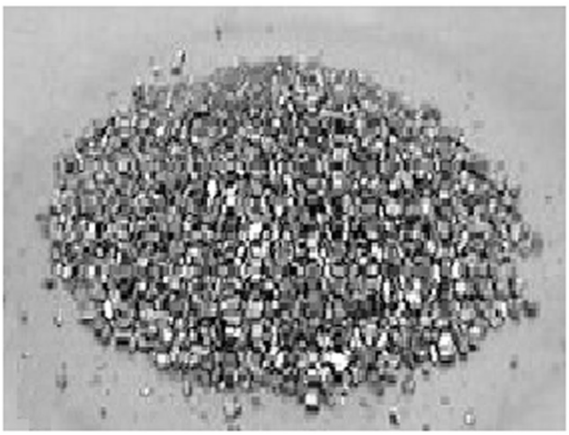

Fig. 1. (a) Tantalum lumped powder for capacitors produced by plasmochemical technology in an arc furnace with argon–hydrogen plasma. Particle size 20–63 μm, specific surface area 160 cm^2/g, bulk density 7.8 g/cm^3 [6]. (b) Niobium hydride, Silmet JSC (http://www.silmet.ee/).

Silmet-Molycorp JSC produces now ground powder of niobium hydride (Fig. 1b) applying the alumothermal technology [6].

This work is an act of scientific cooperation between the Institute of Inorganic Chemistry of Riga Technical University (Salaspils, Latvia), the Institute of Metallurgy of the Russian Academy of Science (Russia, Moscow), and the Chemical Engineering Department of Tallinn University of Technology (Tallinn, Estonia). The studies on the plasmochemical recovery of niobium and tantalum pentachloride were executed on a pilot arc plasmochemical installation of the Institute of Metallurgy of the Russian Academy of Science. These studies were supplemented by the results of pilot tests to install a plasma with a hollow tubular cathode with a capacity of 250 kW (Silmet JSC) [6].

The main goal of this experimental research was to study and optimize the plasmochemical process of the production of tantalum and niobium nanopowders (20–150 nm) from their pentachlorides at pilot scale in the heated up to 3500 K hydrogen stream in a plasmatron.

EXPERIMENTAL AND APPARATUS

The experimental studies and pilot scale tests of niobium and tantalum pentachlorides reduction were carried out in the heated up over 3000 K plasma stream from the arc plasmatron with a power of 15–100 kW. A general view and a scheme of the equipment with a power of 25 kW and metal powder output of 3–5 kg/h is presented in Fig. 2. The amount of the plasma creating gas (mixture of argon and hydrogen) is determined by the construction of the plasmatron and its power. At a power of 15–100 kW the required flow rate of the hydrogen–argon mixture is 1.5–10 m^3/h.

Before switching on the plasmatron all equipment was purged with pure argon (99.99%). The flow rate of hydrogen was adjusted by a rotameter with remote control. The off-gas separated from the metal particles in the filtration system was passed through a Venturi-type absorption system with the basic solution, for example, NaOH solution.

The plasmochemical reduction process can be divided into the following stages: evaporation of the raw material ($TaCl_5$ or $NiCl_5$), mixing of the evaporated precursor with the gaseous stream (plasma), chemical reactions in the gaseous phase, formation of the condensed phase and particles growth, relaxation processes and phase transformations on the surface of the condensed solid particles, and chemosorption processes on the gas–solid interface. The complexity of the chemical reaction control is due to the fact that all physico-chemical processes actually proceed in a single time interval. However, it is possible to distinguish the limiting stage – the reduction reaction of the lower chlorides.

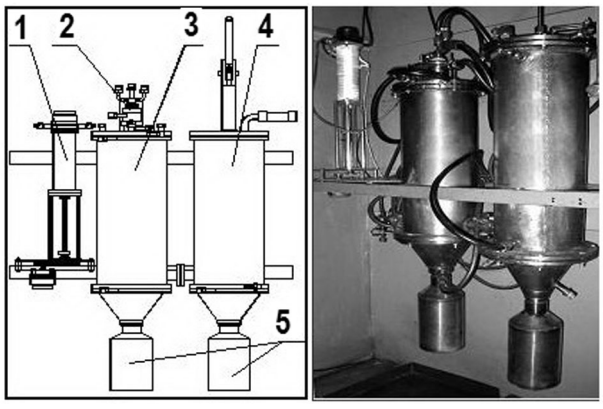

Fig. 2. Schematic installation diagram for the plasmochemical reduction process: 1 – feeder of raw material; 2 – plasma generator; 3 – reactor; 4 – filter; 5 – particle collector.

An important parameter of nanopowders production is the chemical composition of the raw materials. Adjusting the chemical composition of an already produced nanopowder is a very difficult task, thus the purity of the feedstock (niobium and tantalum pentachlorides) was no less than 99.95 mass%. This means that the admixture of metal niobium and tantalum in their chlorides did not exceed 1.2×10^{-2} and 2.5×10^{-2} mass%, respectively. The content of other metal admixtures was less than 10^{-3}–10^{-5} mass%. It is essential to note that the niobium and tantalum chlorides of the required grade are available on the world market without any limitations.

A Transmission Electron Microscope (TEM) JEM-2100 was used to examine the shape and size of the synthesized nanopowders. The structure of the pressurized specimens was studied using a Scanning Electron Microscope (SEM) JEOL JSM-6610LV. The X-ray diffraction patterns (θ–2θ) were obtained using a Siemens D5000 diffractometer. Specific surface area analysis was performed by the nitrogen low-temperature adsorption method (Brunauer–Emmett–Teller (BET) on the analyser Akusorb 2100E (Cultronics) and using a mercury parometer Autopor 9200. The oxidation degree of nanopowders was determined by the thermogravimeter DuPont 1090. The content of hydrogen in nanopowders was determined by the analyser series RHEN (LECO Corporation). For the thermodynamic modelling of the plasma process a licensed computer simulation program HSC Chemistry, elaborated by Outotec Oy, was applied [8].

RESULTS AND DISCUSSION

Thermodynamic modelling of the process

Thermodynamic modelling of the real processes is based on the assumption of the achievement of total thermodynamic equilibrium in the system, which is not always possible in practice. In the present study achievement of local thermodynamic equilibrium in an elementary volume of the plasma stream was assumed [9]. A graphical illustration of the plasmochemical reaction modelling of $NbCl_5$ with hydrogen in the temperature interval 900–5000 K at total pressure of the gas phase of 1 atm is presented in Figs 3 and 4. A summarized reduction reaction of niobium chloride with hydrogen is decribed by the following reaction:

$$NbCl_5 + 2.5H_2 = Nb + 5HCl. \qquad (1)$$

The stoichiometric amount of hydrogen for the reduction of 100 kg of $NbCl_5$ according to this reaction is 1.87 kg. Figure 3 illustrates the impact of temperature on the equilibrium composition of the products in the system Nb–Cl–H. Figure 4 illustrates the equilibrium composition of the compounds in the reaction with

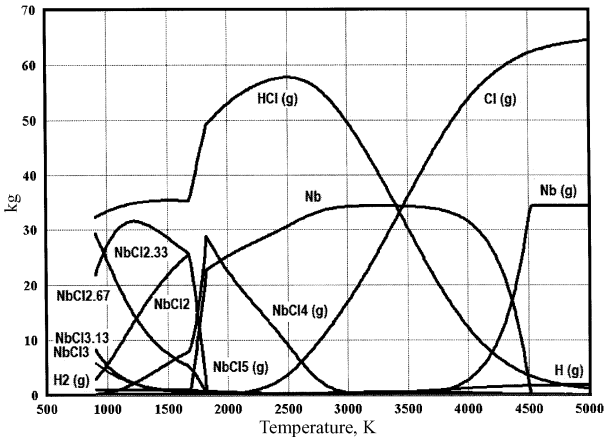

Fig. 3. Impact of temperature on the equilibrium composition of the products in the system Nb–Cl–H. The gaseous state of the compound is indicated by (g) and missing of (g) means the condensed state of the compound.

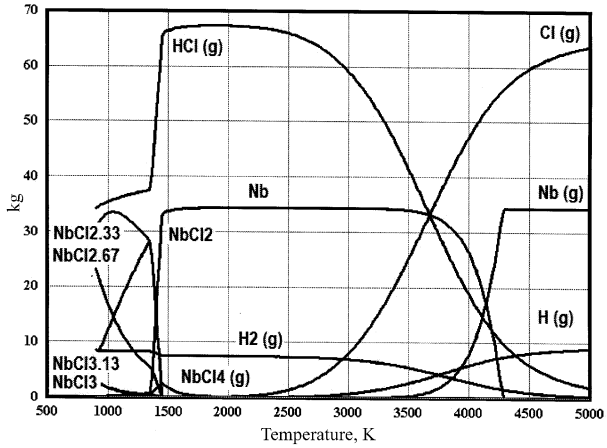

Fig. 4. Equilibrium composition of the compounds in reaction (1) with fivefold excess of hydrogen over its stoichiometric amount. For (g) see legend to Fig. 3.

fivefold excess of hydrogen over its stoichiometric amount.

It can be seen that under the given conditions the process is complicated by the formation of the lower chlorides $NbCl_2$, $NbCl_3$, and $NbCl_4$ and also the subchlorides $NbCl_{2.33}$, $NbCl_{2.67}$, and $NbCl_{3.13}$ till the temperature of 2800 K (at stoichiometric amount of hydrogen). At temperatures higher than 2300–2500 K hydrogen chloride starts to intensively decompose into atomic chlorine and hydrogen. At temperatures over 3500 K metallic niobium starts to evaporate, which decreases its yield in the nanoproduct.

With the increase of the content of hydrogen in the system (Figs 3, 4) up to five- and tenfold excess over the stoichiometry in reaction (1) the area of the temperatures of the formation of lower chlorides and

subchlorides is shifted to 1000–1500 K. The appearance of lower chlorides in the system modelled is an evidence of the stage-wise reduction of $NbCl_5$ according to the scheme:

$$NbCl_5 \rightarrow NbCl_4 \rightarrow NbCl_3 \rightarrow NbCl_2 \rightarrow Nb.$$

From the technological point of view five- to tenfold excess of hydrogen (9.33–18.7 kg per 100 kg of $NbCl_5$) over stoichiometry and temperatures 1700–2000 K are sufficient enough to achieve the full reduction of $NbCl_5$. Under these conditions metallic niobium should practically not be polluted by chlorine in the form of subchlorides. For example, at 2000 K and fivefold excess of hydrogen the computed equilibrium composition of the gaseous phase (in kg) is the following: $NbCl_4$, 5×10^{-2}; $NbCl_5$, 2×10^{-4}; $NbCl_3$, 6×10^{-8}; Nb, 3×10^{-8}. The condensed phase would be formed only by metallic niobium (34.4 kg). According to the computation, a further increase in the hydrogen excess over tenfold would not improve the outcome of the process.

Transformation of niobium and tantalum pentoxides according to reaction (1) in the reductive plasma stream of hydrogen and the production of metallic powders in the form of a condensed dispersed phase are a result of simultaneous complicated physico-chemical processes. Vapours of the raw material (precursors) react with the components of plasma, forming products also in the vapour phase during such a short time interval that the transfer to the solid phase can be conditionally presented as a result of the simultaneous processes of condensation, crystallization, and polymorphous transformations. However, as already mentioned above, the limiting stage of the process is the formation of lower chlorides, whose kinetic parameters have been studied earlier [10].

Conversion of $TaCl_5$ and $NbCl_5$

Inadequate proportions between the physical parameters of the process (amount of pentachlorides, flow rate of hydrogen, temperature in the zone of plasma) lead to an incomplete reduction of chlorides. The concentration of chlorine-containing products in metallic powder increases. To study this phenomenon, the rate of dosing pentachlorides was varied in the range from 1 to 10 g/min.

The results obtained (Fig. 5a) indicated that increasing the pentachlorides dosing rate led to a reduction in the specific surface area of nanopowders. A similar conclusion was reached when the temperature in the zone of the plasma reaction was increased (Fig. 5b). Pilot scale tests enabled optimization of the results of the study [11], and suggest that the temperature regime of the process should be in the range of 2800–3200 K.

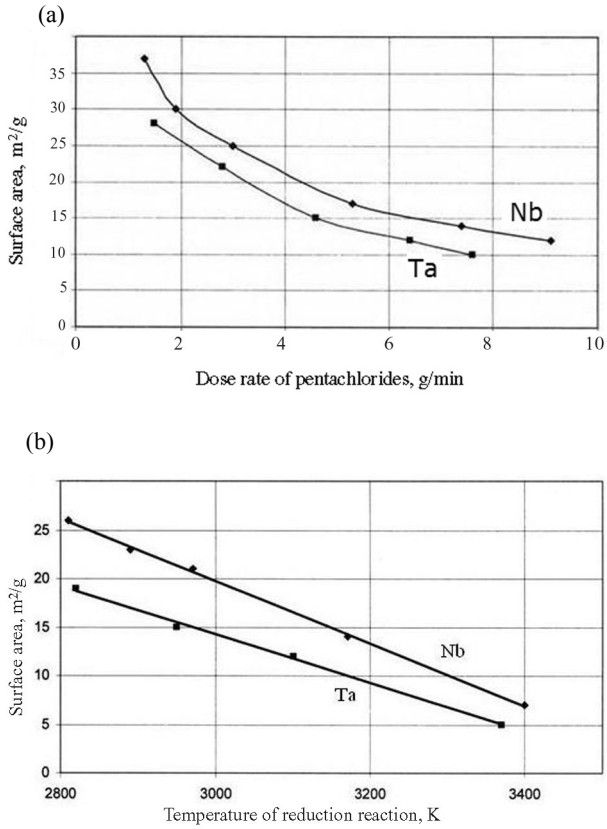

Fig. 5. Dependence of the surface area (m^2/g) of niobium and tantalum powders on the dose rate of pentachlorides (a) and on the temperature of the reduction reaction (b).

Oxygen and hydrogen content

The average content of hydrogen in the nanopowders was 0.01 mass%. Such a relatively low hydrogen content was due to the extremely fast cooling rate of the products at the outlet of the reaction zone, about 10^5–10^7 deg/s. The minimal content of oxygen in the specimens at their removal from the reactor without contact with air was less than 0.3 mass%.

X-ray diffraction analysis of tantalum and niobium nanopowders indicated an insignificant shift of peaks to the side of the smaller divergence angle (Fig. 6). This was obviously due to the formation of hydrides as a result of partial dissolution of hydrogen in the metallic matrix and expansion of the distance between interatoms in the lattice. Modelling using the program HSC Chemistry confirmed this (Fig. 4). It should be noted that the hydration process of compact niobium and tantalum ingots is applied for the production of the so-called debris-type powders. It is possible to reduce the hydrogen content with using annealing under vacuum [12]. After this procedure the content of hydrogen was less than 0.01 mass%, and on the diffraction patterns a reduction in the peaks shift can be followed.

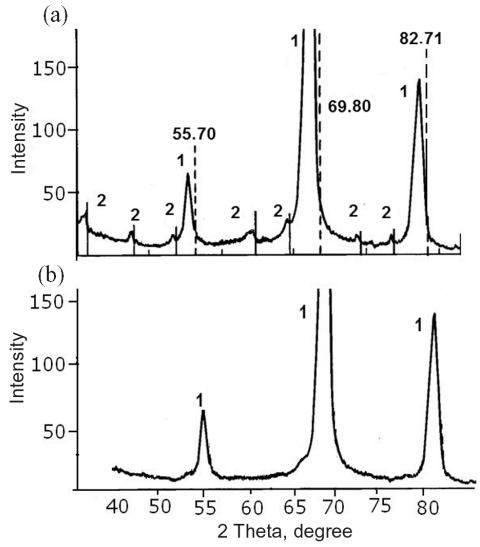

Fig. 6. XRD patterns of the obtained Nb nanopowders. (a) As prepared or initial plasmochemical; (b) dehydrided, i.e. after thermal treatment in argon under vacuum at 1100 K: a – Nb; b – NbO.

On the diffraction patterns (Fig. 6) small peaks of niobium oxides (similarly to tantalum) can be seen. It is possible that some air had infiltrated into the system. Also another source of oxygen is possible. Reaction gases (hydrogen, argon) always contain some amount of oxygen and water. For example, earlier [7] the presence of niobium monoxide in the metal as a result of the above-mentioned factors was found. Our results coincide with the results in [13], whose authors applied X-ray photoelectronic spectroscopy, which enabled them to identify presence of the oxides NbO and N_2O_5 in the surface layer (2–3 nm) of niobium.

Studies on the resistance of plasmochemical powders [7] to oxidation were carried out applying the method of thermogravimetry (TGA) in air at the heating rate of 10 °C/min up to 900 °C (Fig. 7). It is known that

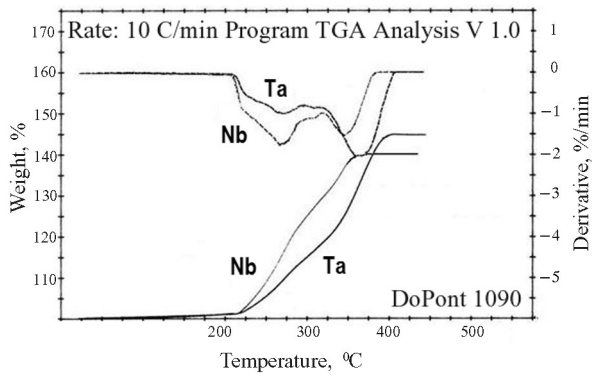

Fig. 7. Thermogravimetric tantalum analysis and niobium powders in air.

niobium, differently from tantalum, forms stable oxides (NbO, NbO_2) and some polymorphic modifications of Nb_2O_5 [14]. This means that the formation of several products and a more complicated reaction mechanism compared to tantalum are possible.

The nanopowders of niobium and tantalum were found to be characterized by the stability of the initial oxidation temperature in the range of 160–170 °C due to the passivation in air. During this period and up to about 200 °C oxygen dissolves in metal and the so-called sub-oxides are formed. The parabolic stage of the oxidation process is relatively short and at the temperature of 220 °C the stage of destructive (accelerated) oxidation starts. The reactions are accompanied by the endo-thermic and exothermic effects. The reaction rate changes twice and in the transfer point the endothermic effect takes place, which is obviously linked to the removal of the remaining hydrogen from the metal lattice. It should be mentioned that the thermal effect of the oxidation reactions of nanopowders diminishes with the reduction of their specific surface area.

On the basis of the difference between the theoretical and the actual mass growth of the specimen it is possible to determine the content of oxygen in the powder. For the powders of particle size of 80–150 nm evacuated from the equipment without air access the content of oxygen does not exceed 0.3 mass%. The oxidation reaction is accompanied by self-ignition. The flame propagation rate across the surface of the powder is over 0.1 mm/s.

Particle morphology and size

Plasmochemical powders of niobium and tantalum are spherical, equiaxial-shaped particles. The polydispersity of the reduced metal powder is due to the radial gradient of temperature in the high temperature zone of the reaction, that is in the zone where metal particles are formed. The growth of the particles across the axis of the plasma discharge proceeds as a result of liquid phase coalescence. Close to the cooled down walls of the reactor a zone of low temperatures is created where the process of coagulation of crystallized particles proceeds much faster leading to the formation of particles with minimum size. The difference between the particles' size can be significant.

Another very important factor in the formation of particles' shape and polydispersity is a recirculating flow in the plasma jet. The turbulence in the stream keeps the particle for a longer time in the central reaction zone and promotes the formation of suitable conditions for its growth. The TEM micrographs in Fig. 8 prove it.

Because of their small size and nonequilibrium conditions of their formation in the arc plasmatrons under conditions of fast cooling metallic nanoparticles have elevated chemical activity. This may evoke self-

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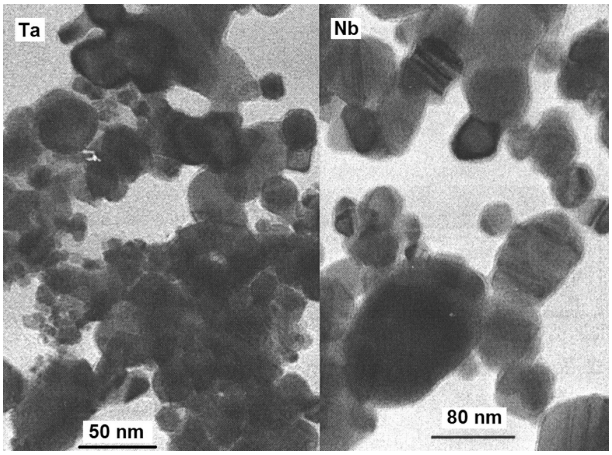

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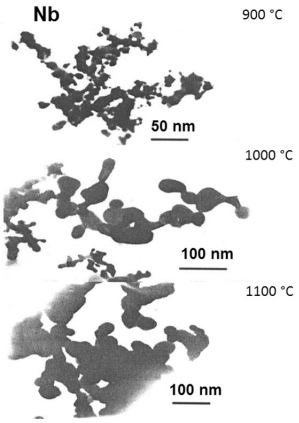

Fig. 8. TEM micrographs: (a) TEM micrographs of Ta and Nb powders; (b) thermally treated Nb powders at different temperatures.

ignition of powders in contact with air oxygen. However, the nanopowders of niobium and tantalum obtained in the reconstruction of pentachloride have a reduced threshold of pyrophoricity due to the adsorbed layer of hydrogen chloride on their surface.

Unfortunately, the large specific surface area of plasma–metal powders of niobium and tantalum (10–40 m^2/g), which is a testament to their good technological qualities, creates problems related to the sorption of hydrogen chloride. The content of hydrogen chloride on the surface of the plasmo-powder extracted from the reactor can reach up to 2 mass%, and therefore, in contact with air, the product absorbs moisture actively, which leads to an oxidation process.

To reduce the content of hydrogen chloride, primary thermal treatment of the powder after the reduction process in the reactor is required. Thermal treatment is implemented in the atmosphere of pure hydrogen or an inert gas at temperatures of 423–473 K during 1 h. As a result, the content of hydrogen chloride is reduced to 0.01 mass%.

With the aim of additional degasation of metal, stabilization of its structure, and correction of the granulometric composition, the impact of thermal treatment at temperatures 1173, 1273, and 1373 K under vacuum was studied. Heating to these temperatures (annealing of powders) was performed at the residual pressure in the vacuum chamber of $< 10^{-3}$ mmHg during 1 h. Thermal treatment led to an additional positive effect: the particles obtained a more regular spherical shape (Fig. 8b). It was established that with raising the annealing temperature the average diameter of particles increased. In [12] a mechanism of recrystallizational growth of niobium particles is discussed. Tables 1 and 2 present the results of the study of physico-technological parameters of plasmochemical powders in comparison with the "debris-form" (or "standard"). Highly dispersed products of plasmochemical reduction visually differ from the "debris-form" powders obtained by hydridation of compact metal. They have a deep black colour and lower bulk density (average 0.10–0.25 g/cm^3).

The chemical composition of the powders is the main parameter that determines their physico-technological properties. For the above-described plasmochemical processes raw materials of high purity were used, which enabled to produce nanopowders with only traces of admixtures: 10^{-3}–10^{-5} mass%. The quality of tantalum powders is illustrated in Table 3. For comparison, impurities of the commercial powder of catalogue number 73-CP-300, FSSS with average particle size of 1.0 ~ 2.5 μm, are presented (http://www.advancedmaterials.us/73MR-0001.htm).

Table 1. Physico-technological properties of Nb powders

No.	Type of powder, temperature	Shape of particles	Surface area, m^2/g (BET)	Average diameter, μm, (BET)	Bulk density, g/cm^3	Flow rate, g/s for d = 5 mm, mass = 50 g	ρ[a]
1	Initial plasmochemical	Sphere	28.4	0.02	0.19	–	0.24
2	1173 K	Sphere	19.4	0.04	0.22	28	0.27
3	1273 K	Sphere	9.6	0.07	0.38	20	0.33
4	1373 K	Sphere	9.1	0.08	0.45	20	0.35
5	"Standard"	Debris	0.09	7.75	3.3	5	0.55

[a] ρ, relative compressibility at a pressure of 50 MPa.

Table 2. Physico-technological properties of Ta powders

No.	Type of powder, temperature	Shape of particles	Surface area, m^2/g (BET)	Bulk density, g/cm^3	Flow rate, g/s for d = 5 mm, mass = 50 g	ρ^a
1	Initial plasmochemical	Sphere	10.5	34	0.19	0.18
2	1173 K	Sphere	8.9	40	0.22	0.21
3	1273 K	Sphere	5.7	63	0.38	0.24
4	1373 K	Sphere	1.83	196	0.45	0.27
5	"Standard"	Debris	0.4	17.4	3.3	0.46

[a] ρ, relative compressibility at a pressure of 50 MPa.

Table 3. Maximum impurities (ppm) of tantalum powders, Capacitor Grade, 99.95–99.98% (metal basis)

Powder	Al	Si	Fe	Nb	Ni	Cr	Ti	W	Mo
Commercial 73-CP-300 (10–25 nm)	10	50	60	50	50	50	5	30	20
Polydispersed (20–150 nm)	3–5	6–10	3–10	80–120	0.3–0.9	3–10	3–5	0.6–1	0.3–1

Pressing (compaction) of niobium and tantalum

It is well known that niobium and tantalum possess excellent plasticity. Presence of oxygen in metal has a negative effect on the deformation of compact and powdered materials. Reduction of particle size of powder promotes an increase in the oxygen content. This causes several problems in powder metallurgy and compression molding. In this study the specimens of nanopowder were compacted on a hydraulic press at 25–200 MPa.

It was found that the powders that had underwent the cycle of thermal treatment were more easily formable in compacting. The increase in the relative density of specimens during compaction was proportional to the pressure (Fig. 9). Details had a regular shape and were not destroyed during extraction from the matrix.

The structure of pressurized specimens was investigated on SEM JEOL JSM-6610LV. The microphoto of a tantalum specimen across its fracture area (Fig. 10) shows that the size of the particles and that of the pores between them are comparable, being about 100 nm.

A sample of tantalum powder with a relative density of 30% was molded after a cycle of thermal treatment at 1173 K. The increase in the relative density during pressing was proportional to the pressure (Fig. 9b).

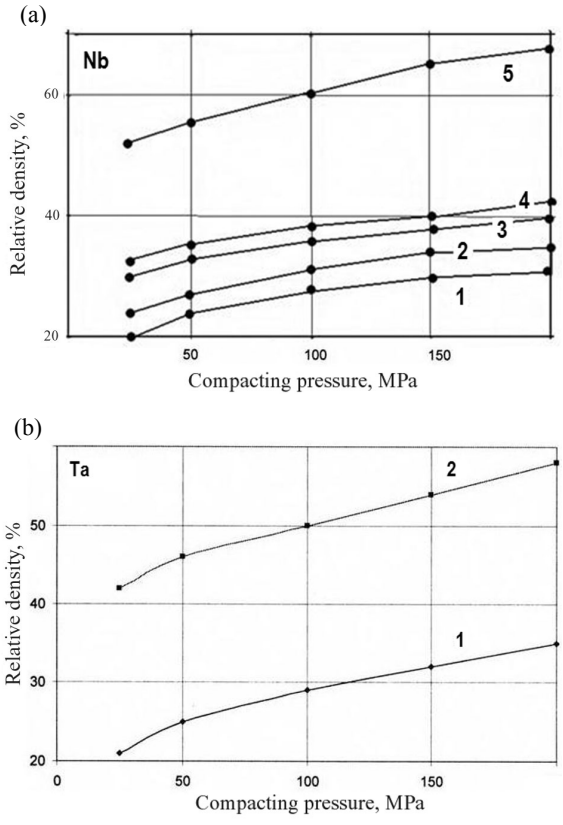

Fig. 9. Effect of compaction pressure on the density of niobium (a) and tantalum (b) samples. Digital indexing schedule matches the serial numbers in Tables 1 and 2.

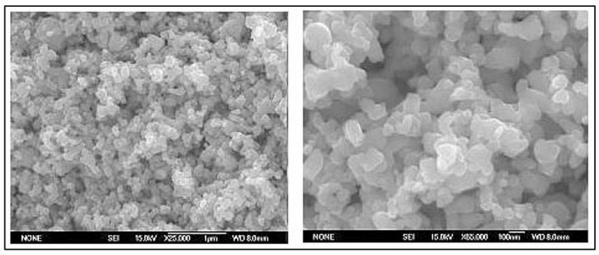

Fig. 10. SEM of a fracture of a tantalum sample at ×25 000 (left) and ×65 000 (right) magnification.

CONCLUSIONS

Studies on the plasmochemical reduction process of niobium and tantalum pentachlorides with hydrogen in arc plasmatrons with an electrical capacity of 15–100 kW resulted in an elaboration of a suitable technological regime for the production of poly-dispersed nanopowders with an average grain size of 20–150 nm.

The temperature was kept in the range of 2800–3200 K. At an electrical capacity of the installation of 25 kW the output of metal was 3–5 kg/h.

The specific surface area of the plasmochemical nanopowders of niobium and tantalum was 10–30 m^2/g. They were of high purity with regard to the metallic admixtures (10^{-3}–10^{-5} mass%). Thermal treatment under vacuum of 10^{-3} mmHg during 1 h or longer resulted in the formation of nanopowders with hydrogen content <0.01 mass%. The content of oxygen in the case the powders were evacuated from the device without air access was less than 0.3 mass%.

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Nioobiumi- ja tantaalinanopulbrite tootmine

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Tänapäeval toodetavad nioobiumi- ja tantaalipulbrid on nanostruktuuriga. Nende peamisteks tarbijateks on telekommunikatsioon, kondensaatorite, mälukaartide ja elektrooniliste skeemide tootmine, implantaatide jt meditsiiniseadmete valmistamine jm. Autorite poolt on uuritud ja katsetatud pilootseadmel reguleeritava suurusega nioobiumining tantaalipulbrite (20–150 nm) tootmist metallide pentakloriididest plasmotronis võimsusega 15–100 kW ja tootlikkusega 3–5 kg metallipulbrit tunnis. Temperatuuri hoiti protsessi käigus piirides 2800–3200 K. Saadud struktuuri stabiliseerimiseks ja granulomeetrilise koostise reguleerimiseks lõõmutati pulbreid vaakumis (jääkrõhk 10^{-3} mmHg) temperatuuril 1373 K üks tund või rohkem. Pulbritel oli suur eripind (10–30 m^2/g) ja need olid suure puhtusastmega (metallilisandeid 10^{-3}–10^{-5}, vesinikku <0,01 ning hapnikku <0,3 massiprotsenti).